Cyclization in amine-cured *N,N*-diglycidylaniline epoxy resins

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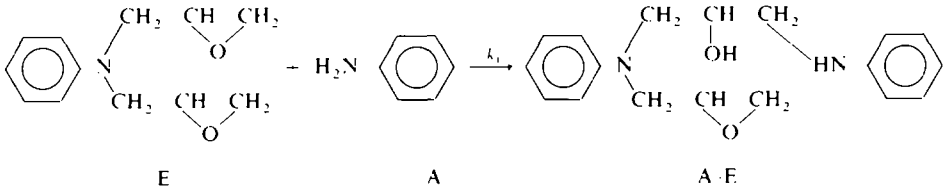
The formation of eight-membered cycles (stereoisomers of 1,5-diphenyl-3,7-dihydroxy-1,5-diazacyclooctane) during the reaction of *N,N*-diglycidylaniline with aniline was followed using high-performance liquid chromatography. The ring compounds were identified by mass spectrometry. The extent of cyclization depends on the ratio of the reaction components, and increases with increasing temperature and upon dilution of the reaction mixture with an inert diluent. The experimental results agree with the theoretical prediction based on the reaction mechanism determined earlier.

(Keywords: cyclization; epoxy resins; kinetics; high-performance liquid chromatography)

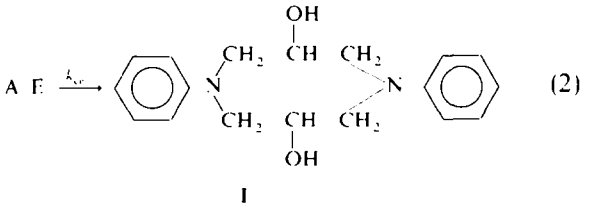
INTRODUCTION

Polyfunctional epoxides based on derivatives of *N,N*-diglycidylaniline, e.g. *N,N,N',N'*-tetraglycidyldiaminodiphenylmethane (TGDDM), were used as matrices of high-performance composites. Aromatic amines, 4,4'-diaminodiphenylmethane (DDM) or 4,4'-diaminodiphenylsulphone usually serve as curing agents. It is well known[1-6] that the mechanism of the reaction of TGDDM with amines differs from that of epoxides based on diglycidyl ether of bisphenol A (DGEBA). Probably the most significant difference is the strong tendency of TGDDM and its derivatives to cyclization[1,3-10], in contrast to DGEBA, in the reaction with amines[7,11,12].

Cyclization was proved to occur in the model bifunctional system *N,N*-diglycidylaniline (DGA or E)–aniline (A). Several types of cycles were isolated from the reaction mixture and identified[8,10,13-15]. The eight-membered ring compound 1,5-diphenyl-3,7-dihydroxy-1,5-diazacyclooctane (I) is formed at the very beginning of the reaction from the adduct A–E by intramolecular addition (equation (2)). The structure and conformation of cycle I was identified using mass, n.m.r. and i.r. spectrometry[8,13]. Attias *et al.*[14] proved the existence of stereoisomers of I in the reaction mixture.

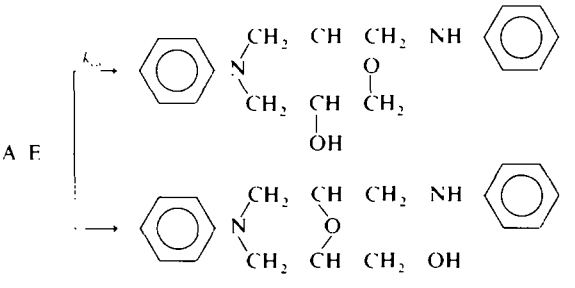


E A A–E (1)



I (2)

Seven- and six-membered rings were shown to arise in a later stage of the reaction, mainly when excess epoxide was used[5,8,10] (equation (3)). Furthermore, tetrahydroquinoline-type cycles were found to be formed[10,15] at temperatures above 150°C.



A–E (3)

The extent of cyclization depends on the relative rates of intra- and intermolecular reactions (see equations (2)–(5)). The study of reaction kinetics in the DGA (E)–aniline (A) system has revealed that the formation of the eight-membered rings I can compete kinetically with intermolecular formation of linear oligomers[5,6]. Intramolecular etherification (equation (3)) is too slow and may be significant only when epoxy groups are in excess. The intermolecular reactions may be written:

$$\text{A–E} + \text{E} \xrightarrow{k_2} \text{E–A–E} \quad (4)$$

$$\text{A–E} + \text{A} \xrightarrow{k_3} \text{A–E–A} \quad (5)$$

where A–E, E–A–E and A–E–A, respectively, are the reaction products with an alternating structure of

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aniline–DGA, DGA–aniline–DGA and aniline–DGA–aniline units.

In polyfunctional systems, cyclization affects the network structure. The theoretical treatment of network formation taking into account cyclization used the cyclic fragments as building units of a polymer structure[16]. Accordingly, a description of the network structure requires knowledge of the concentration of cycles formed during the reaction.

In this paper, the formation of rings **I** and the extent of cyclization have been studied as a function of conversion, temperature, ratio of reaction components and dilution of reaction mixture, using the model system DGA–aniline.

EXPERIMENTAL

N,N-diglycidylaniline (DGA) was synthesized as described earlier[7,17] (99.9% purity according to h.p.l.c.). Aniline was distilled at reduced pressure (99.9% purity by gas chromatography).

DGA was reacted with aniline in sealed ampoules at 100, 140, 160 and 180°C, respectively, either in bulk or in solution. Toluene, diethylene glycol dimethyl ether (DEGDME), triethylene glycol monomethyl ether (TEGMME) or isopropyl alcohol were used as inert solvents. The hydroxyl group of the solvents did not react under the given conditions. Reaction of DGA with aniline proceeded up to full conversion of the minority component; samples were analysed using h.p.l.c. The maximum concentration of ring **I** formed during the reaction was determined.

A Spectra Physics SP 8100 liquid chromatograph with a glass column (150 × 3.3 mm) packed with the reverse phase Separon SIX C18 (particle size 5 μm) (Laboratory Instruments, Prague) was used. Gradient elution (water methanol) was employed starting with 70% water and ending with 100% methanol. Samples (10 μl) were injected as ~1–2% solutions in acetone and detected at $\lambda = 300$ nm.

Cycles were isolated from the reaction mixture by semi-preparative h.p.l.c. with a stainless-steel column (250 × 8 mm) packed with Separon particles (7 μm). Solutions with concentration 10 times higher than in analytical h.p.l.c. were injected (100 μl) repeatedly.

The ring compound **I** was prepared by the reaction of an equimolar mixture of DGA with aniline in toluene solution heated to 135°C for 9 days[8]. The *d,l*-stereoisomer of **I**[14,15] eluted at 24 min (see *Figure 1*) was isolated by crystallization. This isomer was employed for a quantitative calibration of the u.v. detector. The mixture of *l,l*- and *d,d*-stereoisomers[14] was eluted at 27.3 min (cf. *Figure 1*). The u.v. response of all isomers of **I** was assumed to be the same. The ring compounds were identified by means of an AEI MS 902 mass spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows the h.p.l.c. scans of the reaction mixture of DGA with aniline during the reaction. The reaction products corresponding to the peaks 1, 2 and 3 (see caption to *Figure 1*) were isolated by means of semi-preparative h.p.l.c. and identified using mass spectrometric analysis. It was found that products 1 and 3 eluting at 24 and 27.3 min, respectively, correspond to stereoisomers of ring **I** (see 'Experimental' part). Product

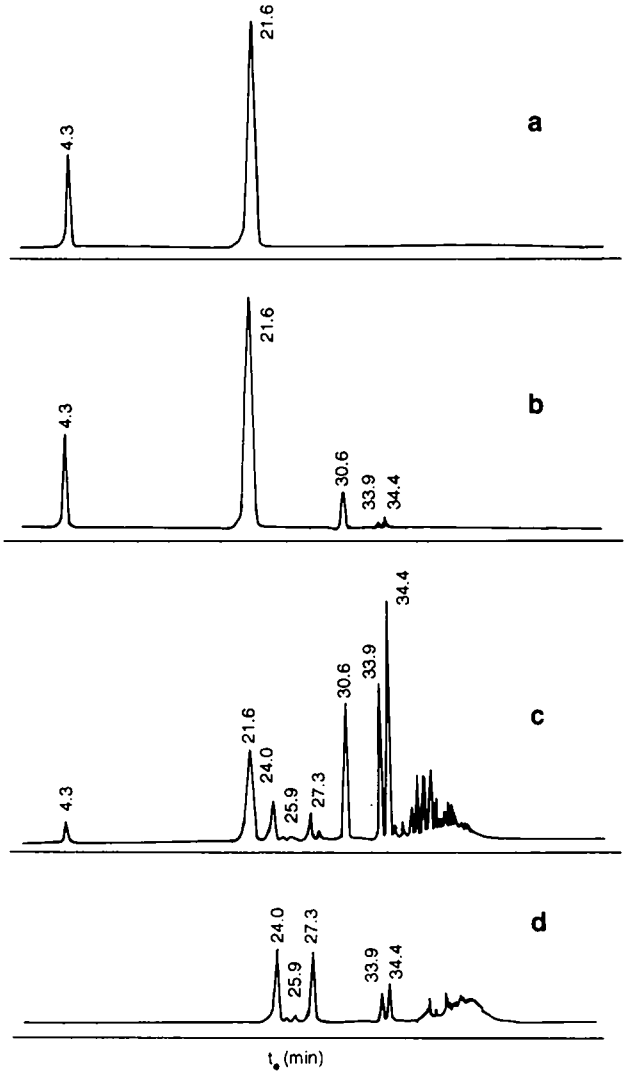
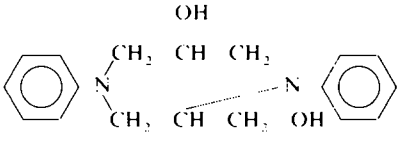


Figure 1 H.p.l.c. scan of the reaction mixture DGA–aniline ($C_{DGA} = 2.94$ M, $C_{anil} = 3.09$ M) diluted with toluene (33 vol%) and reacted at 100°C for time t: (a) $t = 0$ min, (b) $t = 80$ min, (c) $t = 270$ min, (d) $t = 19$ h. Assignment of peaks eluting at times t_e (min): 4.3, aniline; 21.6, DGA; 24.0, isomer of ring **I** (peak 1); 25.9, ring **II** (peak 2); 27.3, isomer of ring **I** (peak 3); 30.6, A–E; 33.9 and 34.4, isomers of A–E–A

2 eluting at 25.9 min was not isolated as a pure substance but was contaminated by product 3. According to the mass spectrometric analysis, it is probably the seven-membered ring **II** containing a primary OH group. The assignment of the other h.p.l.c. peaks is given in *Figure 1*.



II

The kinetic course of the reaction at 100°C is shown in *Figure 2*. The first product formed is the adduct A–E, which is followed by linear oligomers as well as small cyclics (cf. equations (1)–(5)). All isomers of ring **I** are formed at the same time and at a similar rate. Only the sum of the concentrations of these isomers is given in the following figures and has been used to characterize the content of ring **I**, assuming the u.v. response of the

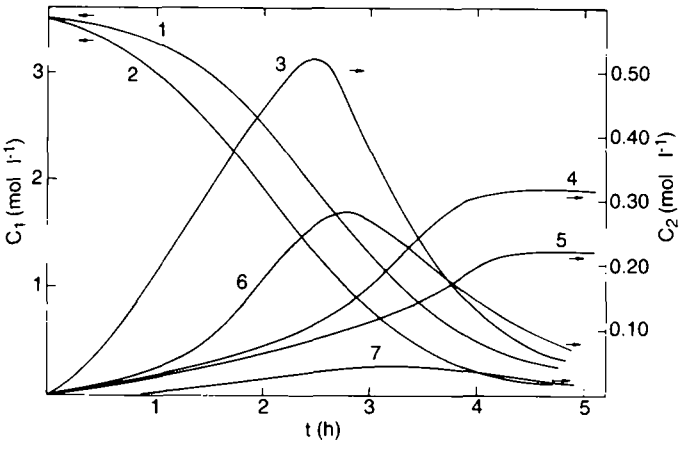


Figure 2 The kinetic course of the reaction of DGA with aniline at 100°C ($C_{DGA} = 3.5$ M, $C_{anil} = 3.5$ M). C_1 and C_2 are the molar concentrations of the initial components and the reaction products, respectively. Curves: 1, DGA; 2, aniline; 3, A–E; 4 and 5, isomers of ring I; 6, sum of isomers of A–E–A; 7, sum of isomers of E–A–E. Curves 6 and 7 are qualitative data only

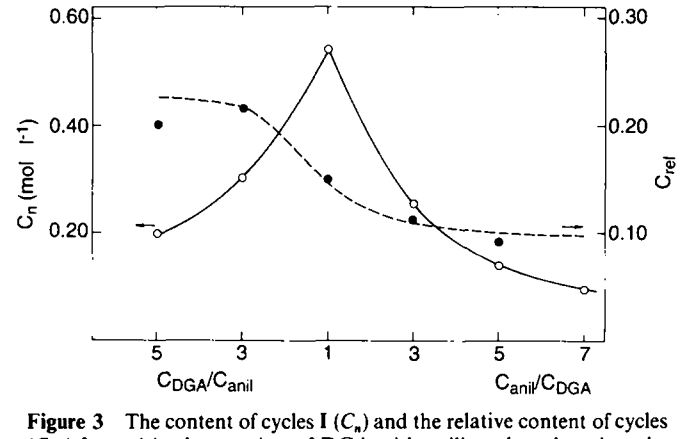


Figure 3 The content of cycles I (C_n) and the relative content of cycles (C_{rel}) formed in the reaction of DGA with aniline plotted against the ratio of reaction components, at $T = 100$°C. $C_{rel} = C_n/C_{min}$, where C_{min} = initial concentration of the minority component. (○) C_n; (●) C_{rel}; the broken curve is the theoretical dependence calculated from the kinetic scheme given in ref. 18

isomers to be the same. The kinetics of formation of higher linear oligomers from smaller ones differs distinctly from the kinetics of formation of the cycles. The content of ring I in the reaction mixture at first increases and then levels off. Apparently, the OH group attached to the rings reacts very slowly at this temperature. Etherification of cyclics is much slower even than that of linear reaction products. Only at higher temperatures ($T > 140$°C) was a decrease in the content of ring I observed after the content had attained the maximum value.

The concentration of cycles I (C_n) in the reaction mixture depends on the ratio of molar concentrations of DGA and aniline, C_{DGA} and C_{anil} (see *Figure 3*). The highest concentration of I was naturally found in the stoichiometric mixture, because I is formed from one molecule of DGA and one molecule of aniline. However, *Figure 3* shows that the relative extent of cyclization increases with increasing excess of the epoxide. The relative extent of cyclization (C_{rel}) is defined as the ratio of C_n and the initial concentration of the minority component (C_{min}), i.e. $C_{rel} = C_n/C_{min}$. The maximum attainable concentration of I is determined by C_{min} because of the stoichiometric composition of I (DGA:aniline = 1:1). The experiments reveal C_{rel} to be quite high, ranging from 8 to 22% in bulk and up to 38% in solution (cf. *Figures 3* and *4*).

The extent of cyclization was also calculated theoretically using the kinetic scheme and rate constants determined earlier[5,6,18]. The content of cycles formed during the reaction is affected by the relative rates of the intermolecular and intramolecular reactions (cf. equations (2)–(5)). The dependence of the extent of cyclization on the ratio of reaction components is determined by the difference in the rates of intermolecular reactions (4) and (5) and their relative rate with respect to the cyclization reaction (2). If aniline is in excess, the intermolecular reaction (5) of the adduct A–E with the primary amino group of aniline prevails (rate constant k_3). This reaction is fast in comparison with intramolecular reaction (2), and the formation of linear oligomers is preferred. On the contrary, in the presence of excess DGA, reaction (4) of the adduct A–E with an epoxy group (rate constant k_2) is more important. This is a relatively slow reaction and the intramolecular reaction is more significant in this case because $k_2 < k_3$ and $k_{Cn}/k_2 > k_{Cn}/k_3$. However, the dependence of cyclization on the ratio of the components is S-shaped (see *Figure 3*). Only small changes in C_{rel} are to be expected at a high excess of one component at $1/3 > C_{anil}/C_{DGA} > 3$. *Figure 3* reveals a quite good agreement of the experimental data with the theoretical curve calculated using the previously determined[6] rate constants: $k_1 = 1.8 \times 10^{-3}$ l^2 mol^{-2} min^{-1}, $k_2 = 0.8 \times 10^{-3}$ l^2 mol^{-2} min^{-1}, $k_3 = 4.0 \times 10^{-3}$ l^2 mol^{-2} min^{-1}, $k_{Cn} = 2.5 \times 10^{-3}$ l mol^{-1} min^{-1}.

The extent of cyclization increases with increasing dilution ($1/\bar{C}$) with an inert solvent (*Figure 4*), where $\bar{C} = (C_A + C_E)/2$ is the average molar concentration of the functional groups, and $C_A = 2C_{anil}$ and $C_E = 2C_{DGA}$ are the concentrations of the amino hydrogen groups and the epoxy groups, respectively. The dependence of the extent of cyclization on dilution was found to be weaker than that predicted by theory. We believe that the disagreement is due to association of OH groups in the reaction products in the non-polar solvent, toluene. The association results in a higher local concentration of reaction components, leading to an increased rate of intermolecular reaction. The intramolecular reaction is not affected by association and, consequently, C_{rel} decreases. The association of reaction products is weaker in a more polar solvent, diethylene glycol dimethyl ether (DEGDME), or in a solvent containing an OH group, triethylene glycol monomethyl ether (TEGMME). It is obvious from *Figure 4* that cyclization is more important in this case. A much better agreement with the theory was found for isopropyl alcohol as solvent.

The decrease in the relative extent of cyclization due to association in apolar solvents was treated empirically by assuming that the relative rate of intermolecular reactions increases as a result of enhanced effective concentration of reagents (C_{ef}). C_{ef} was approximated using an adjustable empirical parameter b_{AS} characterizing the association:

$$C_{ef} = C_S + b_{AS}(1 - S)^{1/2}(C_B - C_S) \qquad (6)$$

where C_S and C_B are the concentrations of functionalities in solution and in a hypothetical bulk mixture with the same ratio of reaction components, respectively, and $S = V_{solvent}/V_{solution}$ is the volume fraction of the solvent

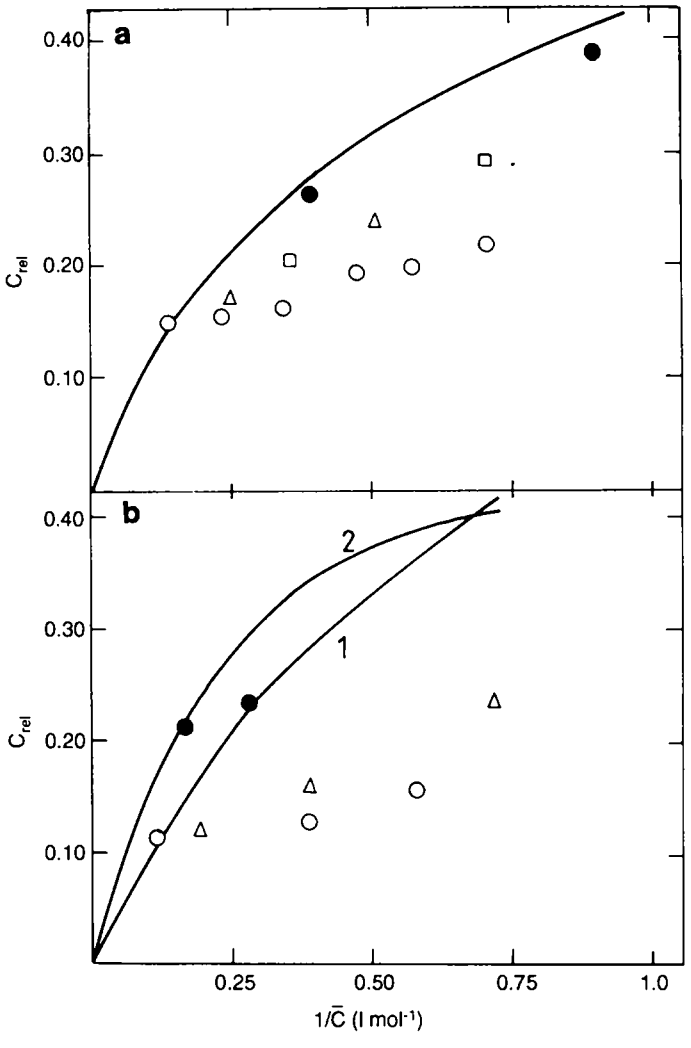


Figure 4 The relative content of cycles (C_{rel}) formed in the reaction of DGA with aniline as a function of dilution with an inert solvent, at $T = 100$°C. Parameters b_{AS} in equation (6): b_{AS}(toluene) = 0.95, b_{AS}(DEGDME) = 0.55, b_{AS}(TEGMME) = 0.4, b_{AS}(isopropyl alcohol) = 0.1. (a) C_{DGA}:C_{anil} = 1:1; (○) in toluene, (Δ) in DEGDME, (□) in TEGMME, (●) in isopropyl alcohol; the full curve is the theoretical dependence. (b) C_{DGA}:C_{anil} = 1:3; (○) in toluene, (Δ) in DEGDME; full curve 1 is the theoretical dependence. C_{DGA}:C_{anil} = 3:1; (●) in toluene; full curve 2 is the theoretical dependence

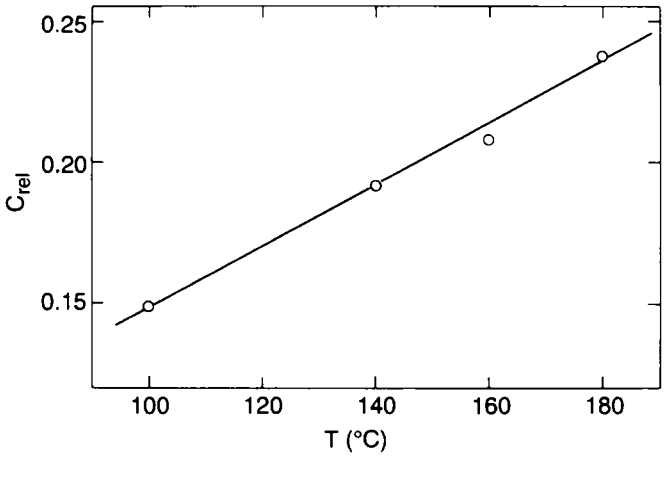


Figure 5 The relative content of cycles (C_{rel}) formed in the reaction of an equimolar mixture of DGA with aniline as a function of temperature. Parameters b_T in equation (7): $b_T = 1.0$ (100°C), 1.49 (140°C), 1.69 (160°C), 2.13 (180°C)

in the reaction mixture. The exponent 1/2 was introduced into the equation in order to fit the experimental data. Thus, $C_{ef} = C_S$ in the absence of association ($b_{AS} = 0$) and C_{ef} approaches C_B in the case of extremely strong association ($b_{AS} = 1$).

The results also reveal an increase in cyclization with increasing temperature (see *Figure 5*) (cf. also ref. 19). A value of 23.8% of cycles was found to be the maximum value of C_{rel} in the reaction of the stoichiometric mixture in bulk at 180°C, compared to 14.9% at 100°C. However, no kinetic data corresponding to the above-mentioned reaction mechanism are available for other temperatures except 100°C. Therefore, to describe the change in the extent of cyclization with temperature, we assumed in the kinetic scheme that the ratio of rate constants for the intramolecular (k_{Cn}) and intermolecular (k_{inter}, i.e. k_2, k_3) reactions, $\kappa = k_{Cn}/k_{inter}$, increased with temperature (see equation (7)). This can be due to a higher activation energy of cyclization (E_{Cn}) as compared with that of intermolecular reactions (E_{inter}). The temperature-dependent adjustable parameter:

$$b_T = \exp\left(\frac{-(E_{Cn} - E_{inter})(373 - T)}{373TR}\right)$$

was used to obtain the best fit with the experimentally determined extent of cyclization at higher temperatures:

$$\kappa_T = b_T \kappa_{100} \qquad (7)$$

where κ_T and κ_{100} are the ratio of rate constants at temperature T and 100°C, respectively, and R is the gas constant.

CONCLUSIONS

The study of the bifunctional system DGA aniline reveals the formation of isomers of the eight-membered ring **I**. The relative extent of cyclization increases with increasing excess of epoxide in the initial mixture, with increasing reaction temperature and with dilution of the reaction mixture. Cyclization, however, is partly suppressed by association of reaction products in non-polar solvents. Cyclization has been treated theoretically using the kinetic scheme determined earlier and empirical parameters that characterize the association in solvents and the effect of temperature.

REFERENCES

1 Byrne, C., Hagnauer, G. L., Schneider, N. S. and Lenz, R. W. *Polym. Compos.* 1980, **1**, 71
2 Gupta, A., Cizmecioglu, M., Coulter, D., Liang, R. H., Yavrouian, A., Tsay, F. D. and Moacanin, J. *J. Appl. Polym. Sci.* 1983, **28**, 1011
3 Morgan, R. J. *Adv. Polym. Sci.* 1985, **1**, 72
4 Grenier-Loustalot, M. F., Cazaux, F., Berecoechea, J. and Grenier, P. *Eur. Polym. J.* 1984, **20**, 1137
5 Matějka, L. and Dušek, K. *Macromolecules* 1989, **22**, 2902
6 Matějka, L. and Dušek, K. *Macromolecules* 1989, **22**, 2911
7 Matějka, L., Dušek, K. and Dobáš, I. *Polym. Bull.* 1985, **14**, 309
8 Matějka, L., Tkaczyk, M., Pokorný, S. and Dušek, K. *Polym. Bull.* 1986, **15**, 389
9 Grenier-Loustalot, M. F., Orozco, L. and Grenier, P. *Eur. Polym. J.* 1987, **23**, 757
10 Attias, A. J., Ancelle, J., Bloch, B. and Laupretre, F. *Polym. Bull.* 1987, **18**, 217
11 Ore, S. and Tjugum, O. G. *Acta Chem. Scand.* 1970, **24**, 2397
12 Luňák, S. and Dušek, K. *J. Polym. Sci., Polym. Symp.* 1975, **53**, 45

13 Reyx, D., Costes, B., Matějka, L. and Dušek, K. *Polym. Bull.* 1988, **19**, 269
14 Attias, A. J., Ancelle, J. and Bloch, B. 'European Symposium on Polymeric Materials, Chemical Aspects in Processing Operations and Use of Polymeric Materials', Lyon, 1987, p. CPA 08
15 Costes, B., Reyx, D. and Platzer, N. *Makromol. Chem.* 1989, **190**, 349
16 Dušek, K. and Matějka, L. 'Biological and Synthetic Polymer Networks', Elsevier, Amsterdam, 1987, p. 335
17 Doskočilová, D., Matějka, L., Pokorný, S., Štokr, J., Březina, M., Dobáš, I. and Dušek, K. *Polym. Bull.* 1985, **14**, 123
18 Matějka, L. and Dušek, K. *Polymer* 1991, **32**, 3195
19 Serrano, D., Peyrelasse, J., Boned, Ch., Harran, D. and Monge, P. *J. Appl. Polym. Sci.* 1990, **39**, 679